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(54) Title: ELASTOMER SEAL (57) Abstract Seals capable of containing corrosive liquid and/or vapor of, e.g., HCFCs, are made of cured blends of (a) CTFE/VF ₂ elastomer, (b) chlorine-free fluoroelastomer, and (c) 1 to 20 wt.% of hydrocarbon polymer, based on the combined weight of (a) and (b). The blends are homogeneous and coherent wherein the hydrocarbon polymer is not visible at 165X magnification as a separate phase within the matrix of the blend of (a) and (b), and the blend is free of internal cracks and voids.		

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TITLE**ELASTOMER SEAL****BACKGROUND OF THE INVENTION**

The present invention relates to fluoroelastomer seals and
5 compositions therefore, for sealing such fluids as fluorocarbons, chlorocarbons,
hydrogen fluoride and hydrogen chloride, and mixtures thereof.

An important use of elastomers is for the production of seals, such as
gaskets and O-rings for sealing fluids. Elastomers generally are able to act as a
seal because of their resilience and general impermeability to many fluids. This
10 is important not only to avoid the loss or contamination of valuable materials,
but also to protect personal safety, health and the environment.

The requirements for a suitable seal are many. First, of course, it
must not degrade or lose its elasticity in contact with the fluids being handled,
even at extremes of temperature and pressure. It must not allow these fluids to
15 pass through them easily by permeation. It must not react with these fluids or
contaminate them with impurities. And the material must not swell appreciably
in contact with the fluids being handled, even at elevated temperatures. For
example, if an O-ring in contact with a moving surface swells appreciably, it
may be extruded into a close-clearance area where it will be torn by friction.
20 When an O-ring swells while in contact with a fluid under pressure or high
temperature, and the pressure or temperature is then reduced, the O-ring may
shrink from its extruded position in a way that causes fluid leakage to occur.

Fluoroelastomeric polymers have been utilized extensively for such
sealing applications because of their outstanding chemical inertness, solvent
25 resistance and their resistance to high temperatures. In such applications their
higher cost than other elastomers is readily justified by their longer life and
superior performance.

However, existing fluoroelastomers are not by themselves suitable
for sealing certain organic fluorochemical fluids under typical conditions.
30 Because of the chemical similarity of fluorochemical fluids to fluoroelastomers,
the fluids tend to dissolve in the fluoroelastomers and thereby cause its swelling
and physical deterioration. When such fluorochemicals are manufactured, many
of the process streams also contain chlorocarbons and highly corrosive
hydrofluoric acid (HF) or hydrochloric acid (HCl), adding to the severity of
35 attack. In particular, 2,2-dichloro-1,1,1-trifluoroethane (HCFC-123) is very
aggressive in surface attack on seals. HCFC-123 has therefore proven to be one
of the most difficult products for which to find a satisfactory seal.

There is a need in the fluorochemical industry for a fluorine-containing elastomeric seal especially suitable for sealing, including containing fluorocarbons, chlorocarbons, hydrogen fluoride, hydrogen chloride and the like, and mixtures thereof.

5

SUMMARY OF THE INVENTION

The present invention satisfies this need by providing a seal comprising cured, coherent, homogeneous elastomer blend comprising (a) chlorotrifluoroethylene/vinylidene fluoride (CTFE/VF₂) elastomer, (b) chlorine-free fluoroelastomer, and (c) a minor proportion with respect to the combined weight of (a) and (b) of hydrocarbon polymer.

10

Surprisingly, the hydrocarbon polymer, although present in a minor amount; e.g., 1 to 20 wt%, based on the weight of components (a) plus (b) in the blend, and although incompatible with the fluoroelastomers, nevertheless imparts a significant reduction in fluorochemical permeability of the seal.

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The present invention also provides the curable, coherent homogeneous composition blend useful for fabrication into the seal and curing. The composition is prepared by compounding components (a), (b), and (c) together with curing agent at elevated temperature; e.g., at least 60°C, but below the curing temperature for the blend.

20

Surprisingly, the hydrocarbon polymer disappears into the resultant composition; i.e., it is not visible as a separate phase in the elastomer matrix under 165 x magnification, whereby the composition is homogeneous in character. In addition, neither cracks nor voids, which would be expected from the presence of component (c) in the incompatible matrix of components (a) and (b), are visible under this magnification, giving the composition its coherent character.

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The seals of this invention are effective in handling the more aggressive fluorochemicals used for refrigeration such as 2,2-dichloro-1,1,1-trifluoro-ethane (HFC-123) and substitutes for CFCs together with other fluorocarbons, chlorocarbons, HF, HCl or mixtures thereof.

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DETAILED DESCRIPTION OF THE INVENTION

The CTFE/VF₂ polymer used to make composition of the present invention, which, in turn, is used to make the seals of the present invention generally contains about 25-50 mol% chlorotrifluoroethylene, the balance being vinylidene fluoride, and is curable to an elastomer. This product is commercially available through 3M as Kel-F® elastomer. The term "elastomer" as used herein means a polymer which exhibits little plastic flow and quick or nearly complete recovery from an extending force. The extending force can

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stretch the polymer to 100% without breaking. After such stretch and being held for 5 minutes and then released, it will retract to within 10% of its original length within 5 minutes after release.

Chlorine-free fluoroelastomer (component b) includes both
5 perfluoroelastomer and hydrogen-containing fluoroelastomer. Examples of chlorine-free fluoroelastomer include tetrafluoroethylene/perfluoro(alkyl vinyl) ether (TFE/PAVE) polymer and vinylidene fluoride/hexafluoropropylene (VF₂/HFP) polymer, curable to elastomer.

With respect to the TFE/PAVE polymer, this polymer contains
10 sufficient PAVE to provide elastomer properties when cured. PAVE includes perfluoro(alkoxy alkyl vinyl)ether (PAAVE). The alkyl group of the PAVE preferably contains 1 to 8 carbon atoms. Preferably the PAVE is perfluoro(methyl vinyl)ether (PMVE) or PAAVE. TFE/PMVE elastomer is available from DuPont and TFE/PAAVE polymer is available from Daikin as
15 Dai-el Perfluor GA-55® fluoroelastomer. The amount of PAVE will generally be about 25 to about 40 mol% PAVE and complementally to total 100 mol% about 75 to about 60 mol% TFE. When less than about 25% of the PAVE is added, the copolymer generally does not exhibit sufficiently elastomeric properties; addition of more than about 40% of the PAVE is difficult.

20 A wide variety of hydrogen-containing fluoroelastomers can be used in this invention. They are copolymers of at least one fluorinated monomer, but may incorporate monomers containing no fluorine. These polymers commonly, but not universally, incorporate vinylidene fluoride (VF₂) as a monomer. The most common fluoroelastomers are copolymers of VF₂ with
25 hexafluoropropylene (HFP) and optionally tetrafluoroethylene (TFE). However, the use of other fluoromonomers and of monomers that do not contain fluorine is well known. Other monomers than can be used include hydrocarbon olefins such as ethylene (E) or propylene (P), and PAVE, as described above. A preferred PAVE is perfluoro(methyl vinyl)ether (PMVE). Fluoroelastomers
30 incorporating such monomers include TFE/VF₂/PMVE, E/TFE/PMVE, and TFE/P copolymers.

The VF₂/HFP polymer is a preferred member of the class of
hydrogen-containing fluoroelastomers. The copolymers generally contain from 70% to 30% by weight of vinylidene fluoride units and from 30% to 70% by
35 weight of hexafluoropropylene (HFP) units. When the fluoropolymer contains less than 30% of HFP units it tends to become non-elastic. Production of a fluoropolymer containing more than 70% HFP is difficult. This polymer is available, for example, as Viton® fluoroelastomer by DuPont.

To provide or enhance curability, fluoroelastomers may include reactive cure site moieties derived from small concentrations of cure site monomers in addition to the primary monomers described above. Such monomers can include, for example, bromine-containing fluoroolefins and fluoro(vinyl ethers), and cyano-substituted fluoro(vinyl ethers). Cure site monomers may be present in concentrations up to about 3 mol%. Alternatively or additionally, chain transfer agents that are not perfluorinated can be used in the polymerization reaction to introduce desirable fragments into the polymer for curing purposes. Such agents include iodinated compounds that result in bound iodine in the polymer, commonly at one or both ends of the molecule. When iodinated compounds are used in polymerization, the resulting concentration of iodine in the fluoroelastomer is at least 0.001 wt%, desirably at least about 0.05 wt%, and preferably at least about 0.1 wt%. The hydrogen-containing fluoroelastomer is generally amine or polyol curable.

The CTFE/VF₂, and chlorine-free fluoropolymers curable to fluoroelastomers, such as the TFE/PAVE and VF₂/HFP polymers described above are typically individually supplied with curing agents and compounding ingredients, such as triallylisocyanurate and/or organic peroxide (curing agents), compounding oil, and reinforcing agent such as carbon black, in amounts ranging from 1-5 wt% (curing agent), 1-5 wt% (compounding oil), and 5-30 wt% (carbon black) based on the total weight of the entire individual polymer composition. Each polymer is in a compoundable form; e.g., gum, so that they may be blended together. Each polymer might have different or the same curing agents and compounding ingredients as compared to the other polymer.

It is important that the compounding ingredients used in the blends of this invention should be free of any ingredient which is reactive with fluorochemical under expected conditions of use; e.g., metal oxides or carbonates such as CaO, PbO, CaCO₃, should not be present if these blends are to be used in contact with HF or HCl.

The hydrocarbon polymer used in the invention (component (c)) generally has sufficient flow at the usual compounding temperature of 60°C-120°C so as to be able to be homogenized into the matrix blend of components (a) and (b). In the case of crystalline hydrocarbon polymers, this is accomplished by relatively low molecular weight for the polymer, e.g., 1,000 to 10,000. In the case of amorphous (elastomeric) hydrocarbon polymers, this is achieved by the polymer having a glass transition temperature (T_g) less than 60°C. Representative hydrocarbon polymers include ethylene and propylene

polymers, such as polyethylene, polypropylene, ethylene/propylene rubbers with or without a third monomer such as a nonconjugated diene (EPDM).

Proportions of components (a) and (b) can vary widely, e.g., 10 to 90 wt% of (a) and complementally to total 100 wt%, 90 to 10 wt% of (b). Both are fluoropolymers and can be readily blended together. Preferably, the proportion of the CTFE/VF₂ polymer will be from about 10 to 50 wt% of the total amount of (a) plus (b). For ease of compression molding, however, it is preferred that the proportion of CTFE/VF₂ polymer be no greater than 20 wt%. When less than 10 wt% of the CTFE/VF₂ polymer is present, the thermal resistance becomes less than desired. Component (b) can be either a single chlorine-free curable polymer or a mixture thereof, such as a mixture of TFE/PAVE polymers, VF₂/HFP polymers or a mixture of both. These weight percents refer to the fluoropolymers but also generally apply to the individual fluoropolymer compositions which contain their respective curing agents and compounding ingredients, which will be in similar proportion with respect to their associated fluoropolymer. Gums which are curable to elastomer are typically made available with curing and compounding ingredients in amounts not disclosed by the supplier and not determinable by analysis, but it is believed that the individual polymer (gum) composition will usually be at least 80 wt% polymer.

The proportion of hydrocarbon polymer will depend on the particular hydrocarbon polymer used and its compoundability at particular concentrations, in terms of achieving coherence and homogeneity of the ultimate blend. This polymer is used in an amount which is a minor amount relative to (a) plus (b) and which is effective to decrease the permeability of the seal to the fluorochemical. Typically this can be achieved by 1 to 15 wt% of the polymer based on the weight of components (a) plus (b), and preferably from about 2 to 10 wt% of the hydrocarbon polymer.

In formulating the curable, coherent, homogeneous compositions of this invention, it is important that the various components be thoroughly mixed. Methods of adding and blending curing agents and compounding ingredients into a polymer are well known in the art. It is usually done on a roll mill in which the first polymer component is placed on a heated pair of rolls to form a band around the roll drum and the other components are added stepwise. Blending is done by cutting the polymer band with a knife and adding the cut portion back to the roll in a different location, a process called crosscutting. Examination of cross sections of compositions of the present invention after compounding and after fabrication into articles such as O-rings and curing, under 165 x magnification surprisingly have shown both the compositions and

cured blends to be coherent and homogenous. Other mixing and blending apparatus suitable for carrying out this process include a Banbury mixer, a mixing extruder, or other devices can be used. After compounding to form the composition, the composition can be placed in a mold under pressure to form the desired shape of the seal, wherein the composition is then heated to cure the composition to obtain the seal as a result thereof. Often this curing is carried out in two steps; first, initial curing within the mold followed by postcure outside of the mold.

The ability of the seal to withstand fluorochemical is generally based on testing of exposure to hydrogen fluoride at elevated temperature and elevated pressure, depending on the test. An HCFC, such as HCFC-123 may also be present. The tests include chemical resistance as evidenced by volume swell and weight gain of the seal. Retention of the elastomeric character of the seal can be judged by the testing for change in hardness. In the latter case, if the seal either increases or decreases in hardness, the seal can fail by virtue of the seal becoming brittle or too soft (respectively).

Testing of Existing Elastomers on Exposure to HCFC-123

As a first step in seeking a suitable seal for fluorochemical such as HCFC-123, existing elastomers were subjected to a mild exposure test, by immersion of the commercially available elastomer in HCFC-123 for seven days at 54°C. Even in this mild exposure test, none of these elastomers were suitable.

In greater detail, each elastomer (compounded and cured) in sheet form was cut into strips 3 x 0.6 x 0.3 cm and each strip was immersed in a horizontally disposed closed 12 ml vial (1.6 cm I.D. x 7.6 cm long) containing 5 ml of the HCFC-123 under the time and temperature conditions mentioned above. Volume swell of each elastomer strip was determined at the end of the seven days' exposure while still immersed in the HCFC-123, by measuring the increase in length of the strip and cubing the resultant ratio of increased length to original length, assuming the swell was uniform in each dimension. The weight gain was measured one hour after the strip was removed from the HCFC-123. The test results are shown in the following Table A.

Table A

Elastomer	% Vol. Swell	% Wt. Gain
Nordel® ethylene-propylene	-12%	-13%
Viton® A fluoroelastomer	63%	44%
Adiprene® L polyurethane	319%	164%
Thiokol® FA polysulfide	7%	4%
Silicone rubber	142%	35%
Buna S styrene butadiene	21%	24%
Polyisoprene natural rubber	143%	28%
Hypalon® chlorosulf. polyethylene	45%	11%
Neoprene® W polychloroprene	37%	27%
Isobutylene isoprene butyl rubber	39%	15%
Buna N acrylonitrile butadiene	61%	59%

5 All the above elastomers were considered unsatisfactory under this mild exposure to HCFC-123 because of excessive volume swell and weight gain. The only sample with a reasonably low swell and weight gain under these moderate temperature conditions was the polysulfide, but it was ruled out because of its known poor resistance to acids and poor mechanical properties including compression set.

10 A second set of immersion tests were carried out on 19 various elastomers in strip form as above in boiling HCFC-123 (30°C) for a period of only 8 hours. Results were as follows:

Table B

Elastomer	% Vol. Swell
Styrene-butadiene rubber	16%
Butyl rubber	33%
Nordel® hydrocarbon rubber	-5%
Adiprene® urethane rubber	238%
NBR nitrile	64%
Hypalon® synthetic rubber	44%
Neoprene polychloroprene	16%
Hydrin® polyepichlorhydrin	33%
Alcryn® hydrocarbon TPE	64%
Hytrel® polyester elastomer	69%
Silicone rubber	110%
Thiokol® FA polysulfide	16%
Thiokol® ST polysulfide	77%
Vamac® ethylene acrylic elastomer	186%
Aflas® TFE/propylene copolymer	120%
Viton® A fluoroelastomer	60%
Viton® B fluoroelastomer	82%
Viton® GF fluoroelastomer	77%
Kalrez® fluoroelastomer	56%

The degree of swell (or shrinkage) in only 8 hours at a relatively low temperature would rule out all these materials for extended use.

5 A series of tests were run on O-rings of different elastomers exposed to a gaseous mixture of HCFC-123 and AHF (anhydrous HF) at 120°C for 168 hours to simulate the exposure encountered in the use of O-rings as seals in chemical process equipment. Further details of this exposure test are given in the general procedure in the Examples. These conditions of exposure (exposure
10 to gaseous chemical mixture for 120°C for 168 hours) in accordance with the general procedure is the Chemical Process Simulation Exposure Test. Seals of the present invention preferably have volume swell of less than 15%, weight gain of less than 15% and change in hardness of less than 15% when exposed to this test, and more preferably less than 10% for each of these parameters. Even
15 more preferably, the % volume swell and weight gain is less than 5% for each parameter. CTFE/VF₂ elastomer Kel-F® 3700 was included in this test despite its known limitations on physical properties. TFE/PAAVE polymer (Dai-el

Perfluoro GA-55®, (hereinafter called GA-55) was also included in this test, along with TFE/PMVE polymer (Kalrez® fluoroelastomer 4079 O-rings), with the results shown in Table C.

5

Table C

Fluoroelastomer	% Vol. Swell	% Wt. Gain	Hardness (DA)		
			Start	End	Change
Kel F® 3700	24.4	12.5	74	68	-6
GA-55	15.1	2.0	81	77	-4
Kalrez® 4079	39.1	28.5	78	70	-8

The GA-55 had a low weight gain, and was relatively good in volume swell and compression set, but not to the desired level. The sample was observed to have some surface blisters, but it was elastic and did not crack when stretched. Two more samples of the GA-55 were made and tested, and all showed the same surface defects. The Kel F® proved to be superior in compression set to the other commercial fluoroelastomers tested, but poor in volume swell. Attempts were made to improve the performance of these three products by reformulating their compounding mix, but little or no improvement was shown.

Thus, fluoroelastomers existing prior to the present invention did not provide seals with adequate sealing capacity and chemical resistance and physical integrity to be economically useful for containing such corrosive materials as HCFCs and HF. Normally, materials that will withstand these materials will also withstand chlorocarbons, CFC's and HCl and hydrocarbons as well and be useful as a seal therefor. Curable blends of the present invention are also useful for other applications such as hose.

EXAMPLES

The following examples are illustrative of the invention, wherein parts are by weight unless otherwise indicated.

General Procedure

The compounding ingredients that were used were carbon black to impart compression resistance to the composite, halocarbon oil to impart dynamic properties, swell control and temperature resistance, Diak® No. 7 (trialylisocyanurate curing agent) as a secondary curing agent, with Luperco® 101XL (organic peroxide curing agent) as the primary peroxide curing agent.

The CTFE/VF₂ polymer was banded on a hot mill at 77°C to 88°C roll temperature for approximately 4 minutes. The carbon black was then

blended into the polymer until incorporated, taking about 7 minutes. The hydrocarbon polymer (polyethylene) was then added, and the mix blended and crosscut until uniform, taking about 3 minutes. Then the Luperco® was added until fully dispersed in the batch, taking another 3 minutes. The halocarbon oil
5 was then added slowly until fully incorporated in the batch, taking about 4 minutes. Finally the Diak® was added, and both sides of the batch were crosscut about seven times to insure uniformity. Then the batch was rolled 5 to 6 times. The time required for Diak® addition and rolling was about 6 minutes. The rubber was then removed from the roll and allowed to cool. The batch
10 temperature when stripped off the roll was about 99°C to 104°C; the mill roll temperature was estimated at 113°C to 118°C. The total mixing time of this first mix (Compound A) was about 25 to 30 minutes.

The second mix was designated as "Compound B," and contained 100 pts of tetrafluoroethylene-perfluoro(methylvinyl) ether copolymer, GA-55,
15 a precompounded gum containing carbon black, oil, and curing agent.

The final blend was composed of various weighed proportions of Compound A and Compound B as will be described in these Examples. Compound B was first pre-blended on the rolls for about 5 minutes to break down the compound and to build the desired mill-roll temperature to about 77°C
20 to 88°C. Then Compound A was added slowly to Compound B on the mill, adding about one-third of the batch each time and crosscutting the blend 2 to 3 times after each addition. After the addition of Compound A was complete, the blend was mixed thoroughly on the mill and crosscut from time to time until the blend was smooth and well blended in appearance. When an adequate mix was
25 accomplished, the blend was rolled on the mill rolls for at least 7 times, and then stripped off the rolls and allowed to cool to room temperature. It was found desirable to let the blend "relax" for at least 12 hours prior to molding to improve the appearance and properties of the finished products.

After rheological testing of the blend to ensure it met desired initial
30 properties, i.e., further compounding was not necessary, it was placed back on the mill for preheating about 4 to 5 minutes, and then stripped off the roll and cut into long strips for feeding to the extruder for preforming into rope. The extruder temperature was about 52°C, with the die temperature about 82°C. A sample of the extruded compound was then examined in the laboratory to make
35 sure it met all required standards. Then O-rings were molded using a 5-minute cure time and 182°C mold temperature. The O-rings were then oven cured for 16 hours at 150°C. Oven curing resulted in optimum physical properties, a

tighter cure and for the liberation of hydrogen fluoride gas and peroxide radicals from the product.

After this preparation of O-rings, the following tests were run:

Physical properties were measured using Monsanto Tensometer T.10 to confirm
5 that the tensile strength, elongation and modulus were comparable to that which
is desired for O-rings, to qualify the O-rings for the more vigorous chemical
exposure tests. The Shore "A" hardness was measured using ASTM Method
D-2240. Cross sections of the O-rings were cut and viewed under 165X
10 magnification to reveal homogeneity and absence of voids or cracks in the
blends making up the O-rings.

Chemical resistance was determined as follows: Two samples of
each composition of size 214 O-ring were tested by exposure to HCFC-123 for
70 hours at 150°C as described below.

After the initial weight was taken on the latter two O-rings in both air
15 and water, the five specimens were suspended on a hang wire in a tightly closed
bomb. One-sixth of the bomb volume was filled with HCFC-123, making sure
that the O-rings were not immersed, and the bomb was placed in the oven at
150°C. Since the HCFC-123 will be converted to gas when the bomb is heated
to the oven temperature, this procedure ensured that the O-rings were exposed
20 only to the gas phase, not the liquid phase. After the 70-hour exposure test, the
bomb was removed from the oven and allowed to cool for one hour at room
temperature. The previously weighed samples were then reweighed, taking
special care to be fast and accurate since the HCFC-123 will volatilize from the
O-ring in a short period of time. The volume change and weight change were
25 measured using ASTM Method D-471.

Example 1

The following blends were made and fabricated into O-rings
following substantially the general procedure as described above.

Ingredient	Composition - Wt. %					
	1	2	3	4	5	6
TFE/PAVE GA-55	75.00	75.00	75.00	75.00	50.00	25.00
CTFE/VF2 (Kel F® 3700)	15.92	14.97	14.13	13.37	27.03	42.86
EPDM (Vistalon® 404)	-	-	-	-	6.76	4.76
Polyethylene (AC-Poly 617A)	1.59	2.99	4.24	5.35	-	-
N-990 Carbon Black	6.37	5.99	5.65	5.34	13.51	23.81
Halocarbon Oil	0.48	0.45	0.42	0.40	1.01	1.43
Diak® #7	0.32	0.30	0.28	0.27	0.68	0.95
Luperc® 101XL	0.32	0.30	0.28	0.27	1.01	1.19

Test results for these compositions are given in succeeding Examples.

Example 2

Compositions 1 and 2 were fabricated into O-rings following substantially the same general procedure as described in the general procedure, and they were then exposed to a gaseous mixture of chlorodifluoroethane (HCFC-22) refrigerant and anhydrous hydrofluoric acid (AHF) at 50°C for a period of 198 hours using the general procedure and giving the results shown in the following Table:

Composition	% Vol. Swell	% Wt. Gain	Hardness (DA)		
			Start	End	Change
1	4.3	2.9	83	85	2
2	3.7	2.6	89	86	-3

The blends showed superior performance.

Example 3

The procedure of Example 2 was followed except for the following change: composition 1 was exposed to a gaseous mixture of 2,2-dichloro-1,1,1-trifluoroethane (HCFC-123) and anhydrous hydrofluoric acid (AHF) at 120°C for a period of 198 hours.

O-rings of Composition 1 exhibited a volume swell of only 13.5%, weight gain of only 12.2%, and the initial hardness of 79 increased by a small amount to 82, a change of 3 units.

Example 4

The procedure described in Example 2 was substantially repeated except for the following change: Elastomer O-rings were exposed to gaseous

HCFC-123 cycled at room temperature to 30°C (boiling) temperature for 865 hours.

Composition	% Vol. Swell	% Wt. Gain	Hardness (DA)		
			Start	End	Change
1	1.5	1.1	87	85	-2
2	0.2	0.5	89	85	-4
3	0.7	0.9	88	84	-4
4	2.1	1.6	88	85	-3
5	1.2	0.7	84	85	1
6	2.4	1.7	84	83	-1

- 5 The O-rings of all of these cured compositions exhibited low volume swell, low weight gain and small changes in hardness.

Example 5

- 10 The procedure of Example 2 was substantially followed except for the following change: Elastomer O-rings were exposed to (immersed in) liquid anhydrous HF at 100°C temperature for 170 hours.

Composition	% Vol. Swell	% Wt. Gain	Hardness (DA)		
			Start	End	Change
1	2.5	3.0	85	86	1
2	5.9	4.0	85	87	2

Again, the blends showed superior performance.

15 Example 6

The procedure of Example 2 was substantially repeated except for the following change: Elastomer O-rings were exposed to gaseous hydrochloric acid (HCl) at 120°C temperature for 205 hours.

Composition	% Vol. Swell	% Wt. Gain	Hardness (DA)		
			Start	End	Change
1	1.5	1.5	90	87	-3
2	2.5	1.5	87	85	-2
3	1.8	1.5	83	85	2
4	2.0	1.5	85	86	1
5	2.4	1.7	84	84	0
6	2.5	1.7	87	84	-3

In this test, the blends gave satisfactory performance.

Example 7

- The procedure of Example 2 was followed except for the following
- 5 change: Elastomer O-rings were exposed to gaseous perchloroethylene (PCE) at 122°C (boiling) temperature for 840 hours.

Composition	% Vol. Swell	% Wt. Gain	Hardness (DA)		
			Start	End	Change
1	5.2	4.2	85	82	-3
2	6.1	4.9	88	84	-4

In this test, the blends gave satisfactory performance.

10 Example 8

- The following two elastomer blends were fabricated into O-rings as described in the general procedure. Composition 7 was modified from Composition 1 by substituting TFE/PMVE compounded gum which is curable to Kalrez® fluoroelastomer 2035 O-rings for GA-55, and Composition 8 was
- 15 modified from previous Composition 5 by substituting Viton® B fluoroelastomer for GA-55.

Blend Composition (% by weight)		
	Composition	
Ingredient	7	8
TFE/PMVE	75.00	-
Viton® B	-	50.00
Kel F® 3700	15.92	27.03
Vistalon® 404 EPDM	-	6.76
AC Poly 617A	1.59	-
N-990 Black	6.37	13.51
Halocarbon Oil	0.48	1.01
Diak® #7	0.32	0.68
Luperco® 101XL	0.32	1.01

These two compounds were then exposed to gaseous HCFC-123 at 35°C boiling temperature at a slightly superatmospheric pressure for a period of 216 hours, otherwise following the procedure of Example 2, giving the

5 following results:

			Hardness (DA)		
Composition	% Vol. Swell	% Wt. Gain	Start	End	Change
7	8.3	5.5	98	92	-6
8	15.4	14.1	83	71	-12

Performance of these modified blends was also satisfactory for many applications.

WHAT IS CLAIMED IS:

1. Seal of cured coherent, homogeneous elastomer blend comprising (a) CTFE/VF₂ elastomer, (b) chlorine-free fluoroelastomer, and (c) a minor proportion with respect to the combined weight of (a) and (b) of hydrocarbon polymer.
5
2. Seal of claim 1 wherein said fluoroelastomer is perfluoroelastomer.
3. Seal of claim 1 wherein said elastomer is VF₂/HFP elastomer.
4. Seal of claim 1 wherein said elastomer is TFE elastomer.
- 10 5. Seal of claim 4 wherein said elastomer is TFE/PAVE elastomer.
6. Seal of claim 5 wherein said PAVE is perfluoro(alkoxy alkyl vinyl) ether or PMVE.
7. Seal of claim 1 wherein said blend has volume swell of less than 15%, weight gain of less than 15%, and change in hardness of less than 15 when
15 subjected to the Chemical Process Simulation Exposure Test.
8. Seal of claim 1 wherein the weight proportion of (a) and (b) is 10 to 90 wt% of (a) and complementally to total 100 wt%, 90 to 10 wt% of (b).
9. The seal of claim 1 wherein the amount of hydrocarbon polymer is 1 to 20 wt% based on the combined weight of (a) and (b).
- 20 10. The seal of claim 1 wherein said hydrocarbon polymer is ethylene or propylene polymer.
11. Curable, coherent, homogeneous blend comprising (a) curable CTFE/VF₂ polymer curable to elastomer, (b) chlorine-free fluoroelastomer curable to elastomer, and (c) a minor proportion of hydrocarbon polymer.
- 25 12. Process comprising compounding curable (a) CTFE/VF₂ polymer curable to elastomer, (b) chlorine-free fluoroelastomer curable to elastomer, and (c) hydrocarbon polymer to form a coherent, homogeneous blend thereof.
13. Process of claim 12 and additionally forming said blend into an
30 article and curing said article of said blend.
14. Process of claim 13 wherein said article is a seal or hose.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 95/06874

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C09K3/10 C08L27/12 //(C08L27/12,27:12,23:02)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C09K C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US-A-4 948 830 (JON W. MARTIN ET AL.) 14 August 1990 see the whole document ---	1-4,8-14
A	GB-A-1 120 131 (RAYCHEM LIMITED) 17 July 1968 see page 2, line 22 - line 44; claims; examples 4,5 ---	1
A	DE,A,21 55 375 (MINNESOTA MINING AND MANUFACTURING CO.) 18 May 1972 see page 5, line 29 - line 33; claims; examples -----	1-13

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

8 September 1995

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 95/06874

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-4948830	14-08-90	NONE	
GB-A-1120131		NONE	
DE-A-2155375	18-05-72	BE-A- 774900	04-05-72
		CA-A- 954648	10-09-74
		FR-A- 2113544	23-06-72
		GB-A- 1354154	05-06-74
		US-A- 3723577	27-03-73